Strontium Interactions in Hyperalkaline Aluminate Systems

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INTRODUCTION

Strontium-90 is a major radionuclide in spent nuclear fuel, high-level radioactive wastes resulting from the processing of spent nuclear fuel, and radioactive wastes associated with the operation of nuclear reactors and fuel reprocessing plants.

Strontium-90 is of concern to humans and the environment because of its moderately long half-life (29.1 years), its potential for concentrating in bone tissue, and its relatively high energy of beta decay.

High concentrations of aluminum exist in the radioactive waste held in leaking tanks at the United States Department of Energy's Hanford Site in Washington State.

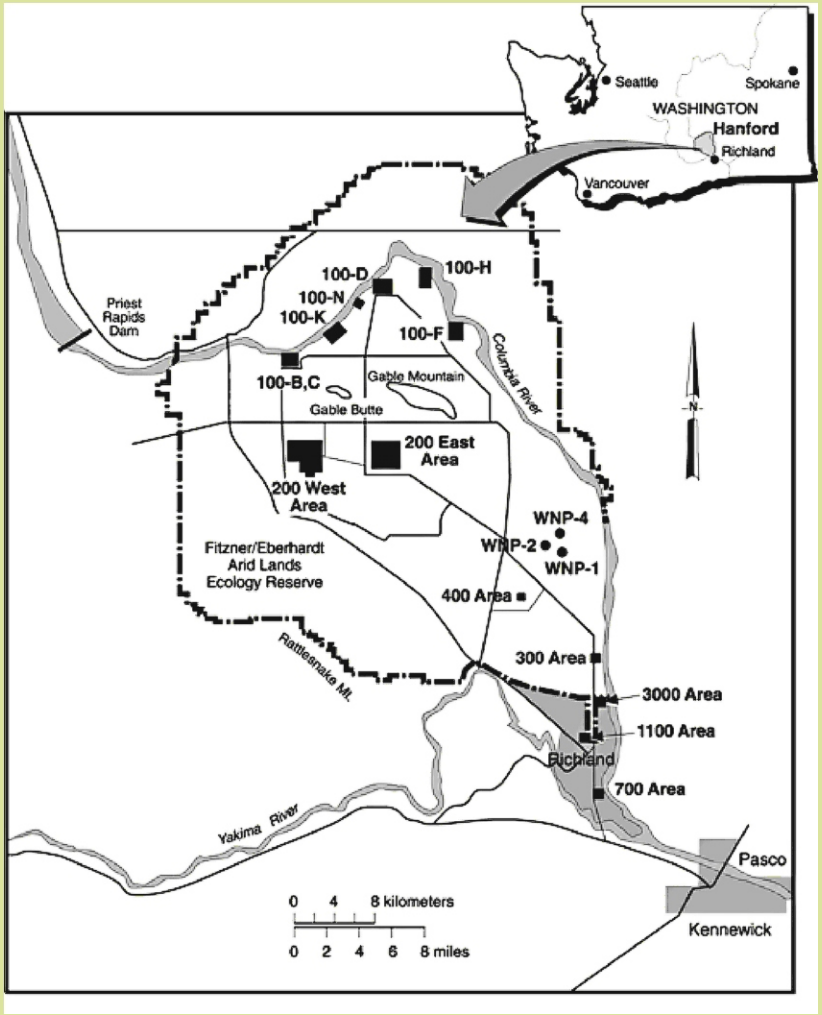


Figure 1. DOE's Hanford Site in Washington State

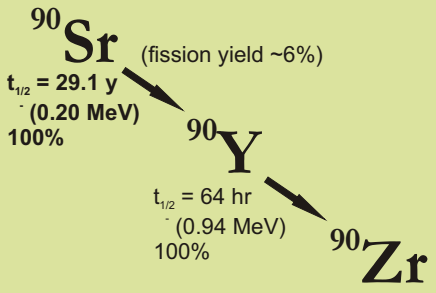


Figure 2. Decay scheme of ^{90}Sr

The aluminum originated from the REDOX chemical processing techniques applied to the waste, which is also the source of the high concentrations of sodium hydroxide, responsible for the extreme alkalinity of the waste. The waste is held in large subsurface tanks, a number of which are leaking into the surrounding groundwater and soils. There is concern about the fate and transport of radionuclides in these leachates and their interactions with components of the vadose zone.

Due to the high aluminum concentrations, one possibility is that aluminum gels immediately precipitate from leaking solutions and that these gels act to sequester radionuclides contained in the waste, such as ^{90}Sr.

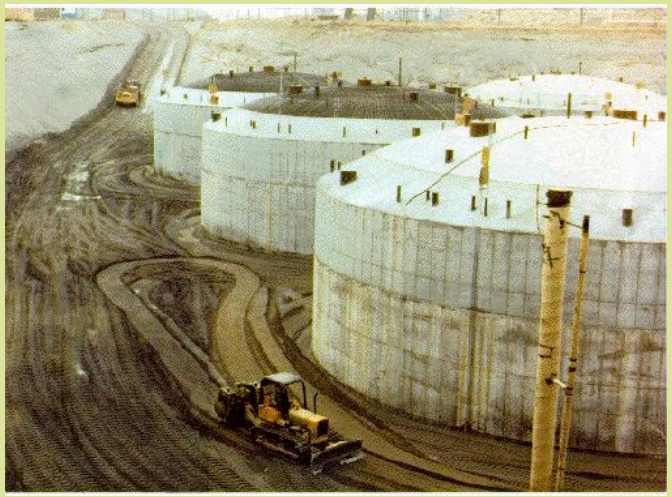


Figure 3. Hanford double shell tanks under construction

This study focuses on the nature of the aluminum solids that precipitate from high aluminum concentration and high pH solutions and how these precipitates change upon aging. In addition, we compare the sorption-desorption characteristics of strontium of these aluminum gel systems to the same properties on aluminum hydroxide powders, such as gibbsite, bayerite, and boehmite. Synchrotron-based spectroscopic techniques (Al K-edge XANES) along with x-ray diffraction are used to characterize the aluminum hydroxide solids that form from solution. Strontium K-edge EXAFS is used to identify the local chemical structure of the predominant Sr interfacial species in the aluminum gel systems.

EXPERIMENTAL

ALUMINUM GELS:

Aluminum gels were made by adding 10 *N* NaOH at an injection rate of 60 mL/hr to solutions of aluminum nitrate (0.1 and 0.5 *M*) and sodium nitrate (10 m*M* and 2 *M*). Hydroxide-to-aluminum mole ratios of 2.8, 3.0 and 3.2 (corresponding to pH values of approximately 4, 6 and 11) were compared at all aluminum and background sodium nitrate solution concentrations. The gels were aged in suspensions at room temperature and 80° C.

CHARACTERIZATION OF ALUMINUM GELS:

Fresh and aged gels were analyzed by x-ray diffraction, laser Raman spectroscopy (not shown here), Al K-edge XANES and Sr K-edge EXAFS (those gels which were doped with strontium and strontium/cobalt). The gels were rinsed with distilled water prior to analysis and allowed to air-dry. Al K-edge XANES (1559.6 eV) were collected on beamline 3-3 at the Stanford Synchrotron Radiation Laboratory(SSRL) using a channeltron to detect the total electron yield and calibrated against Al foil.

STRONTIUM UPTAKE ON ALUMINUM GELS AND POWDERS

Strontium sorption experiments on Al gels and Al hydroxide powders (boehmite, bayerite and gibbsite) at a range of background concentrations of sodium nitrate and pH values were conducted. Strontium uptake and the extent of aluminum dissolution were measured using ICP analysis.

XAS EXPERIMENTS:

Sorption samples were analyzed as wet pastes using EXAFS spectroscopy. Sr K-edge EXAFS were collected on beamline 4-3 at SSRL with a Si 220 monochromator crystal and using a solid-state 13 element Ge fluorescence detector.

RESULTS AND DISCUSSION

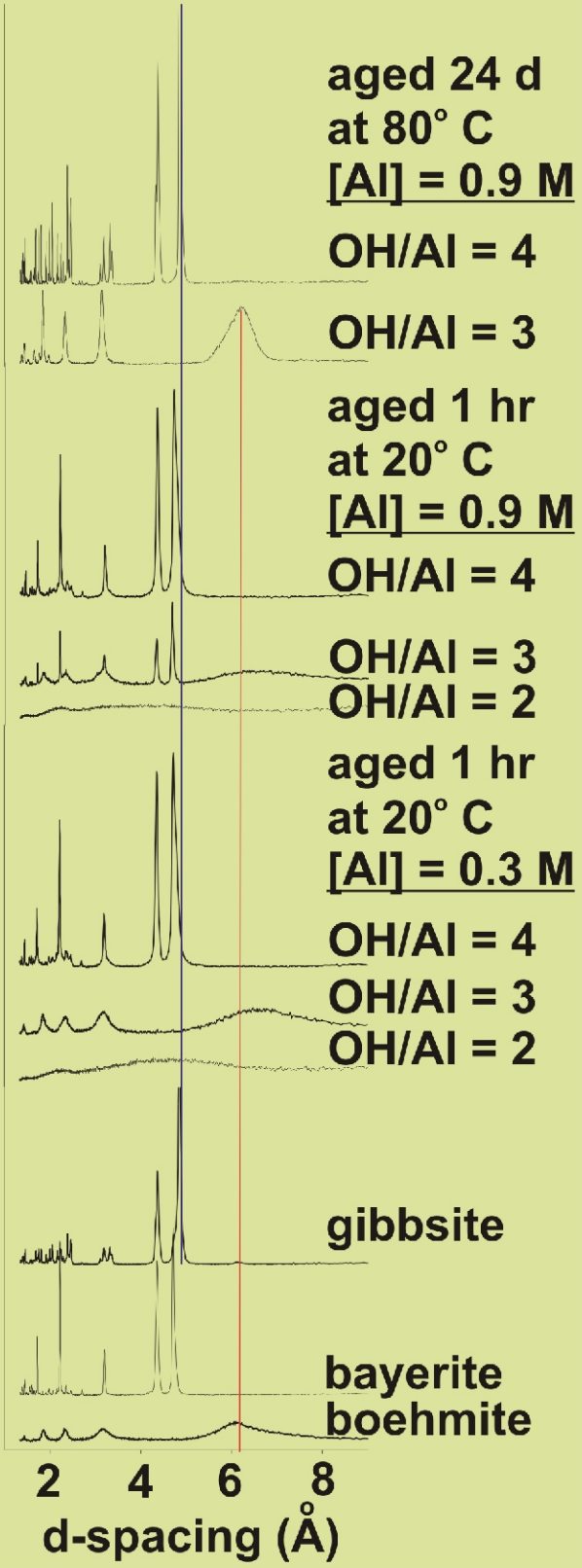
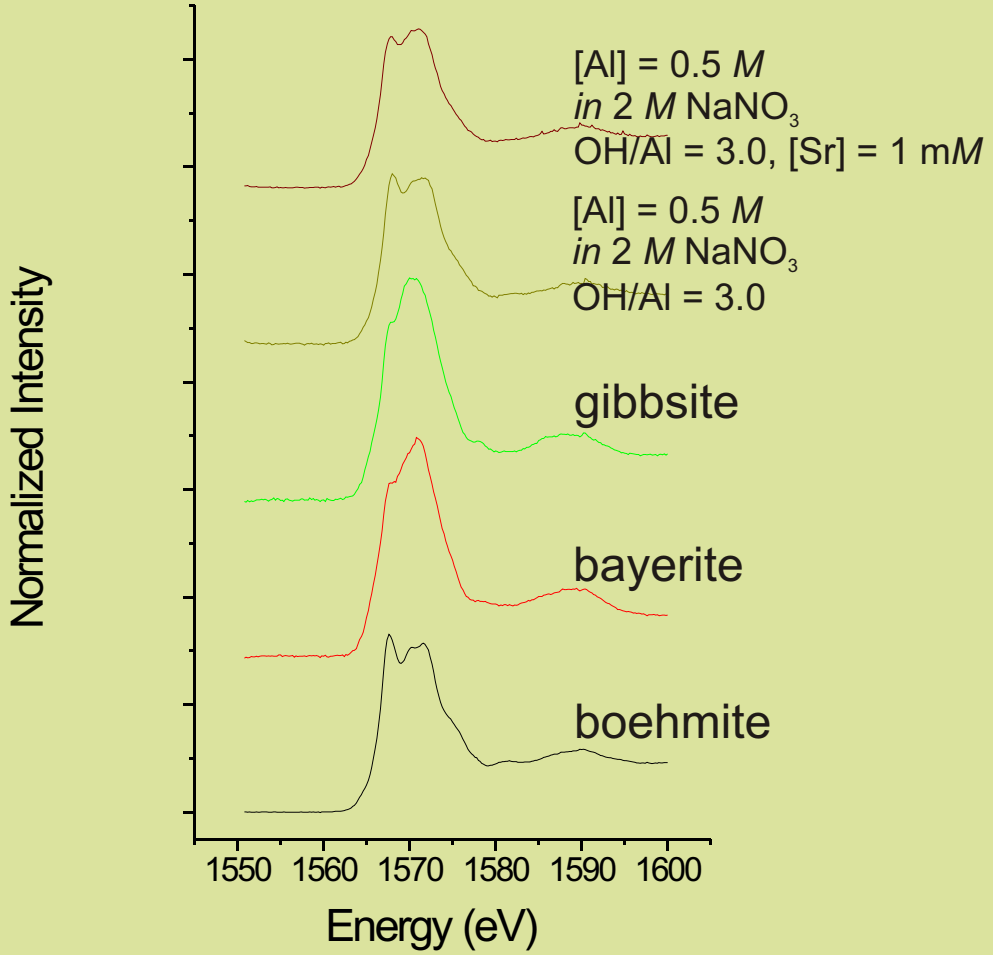


Figure 4. XRD patterns of freshly-precipitated and aged Al gels.

RESULTS AND DISCUSSION

Figure 5. Al K-edge XANES of air-dried Al gels and model Al hydroxide powders



RESULTS AND DISCUSSION

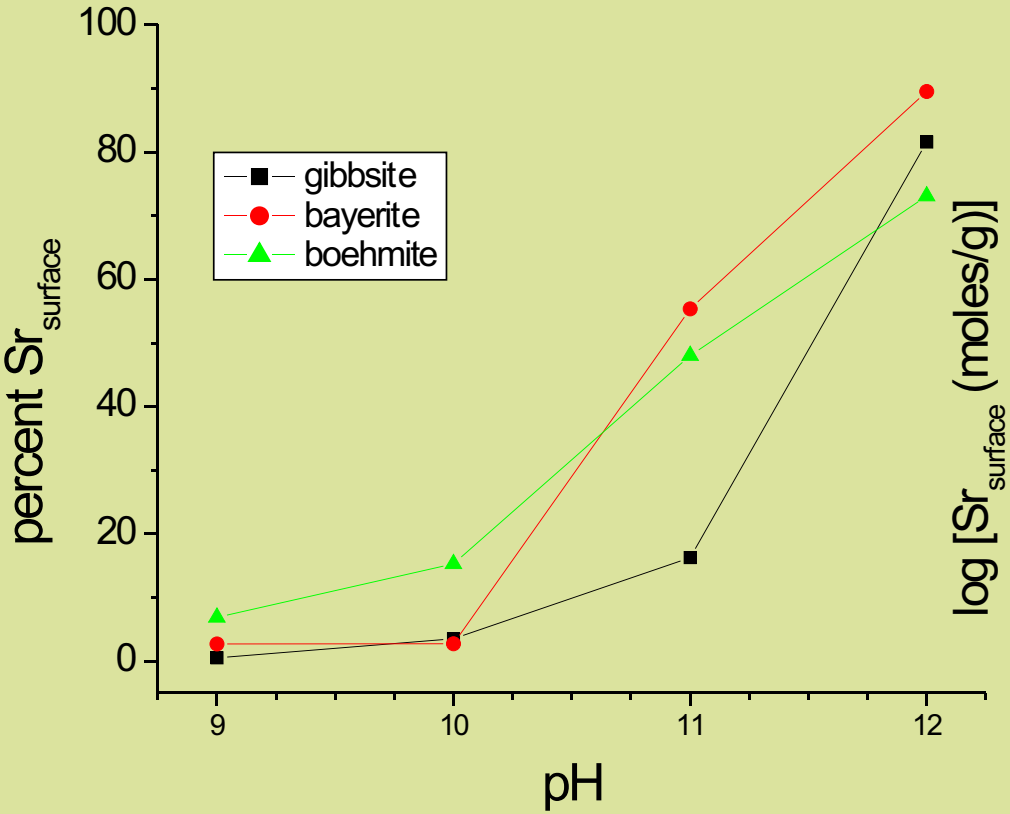


Figure 6. Changes in Strontium sorption on Al hydroxide powders (gibbsite, bayerite and boehmite) as a function of pH.

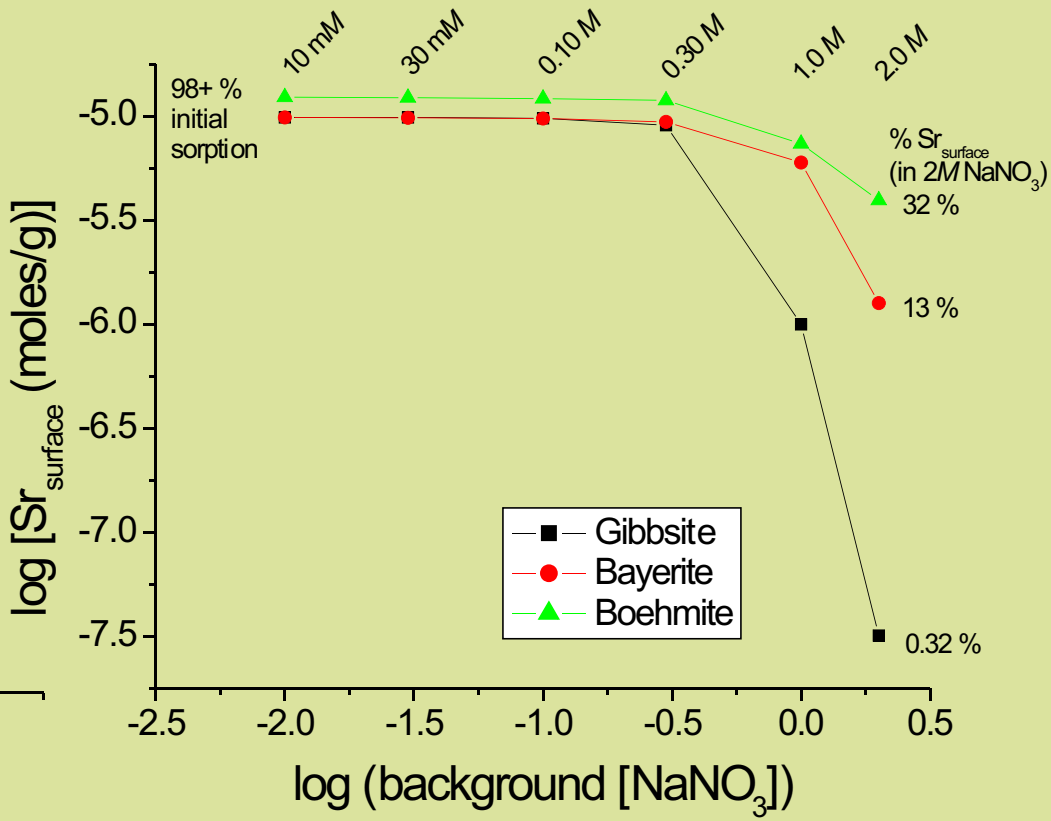


Figure 7. Changes in Strontium sorption on Al hydroxide powders (gibbsite, bayerite and boehmite) as a function of sodium nitrate concentration at pH 10.

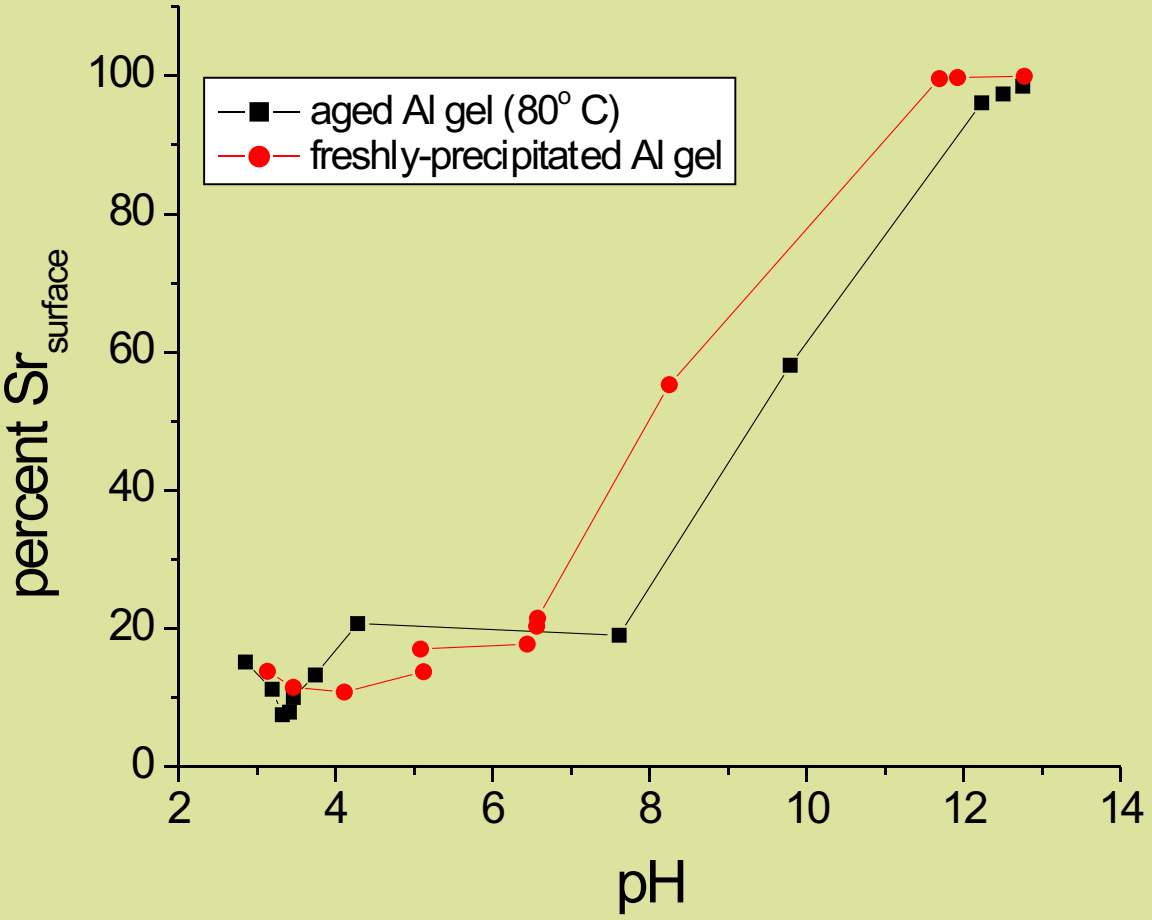


Figure 8. Comparison of Strontium sorption on freshly-precipitated Al gels and aged Al gels (5 days at 80° C).

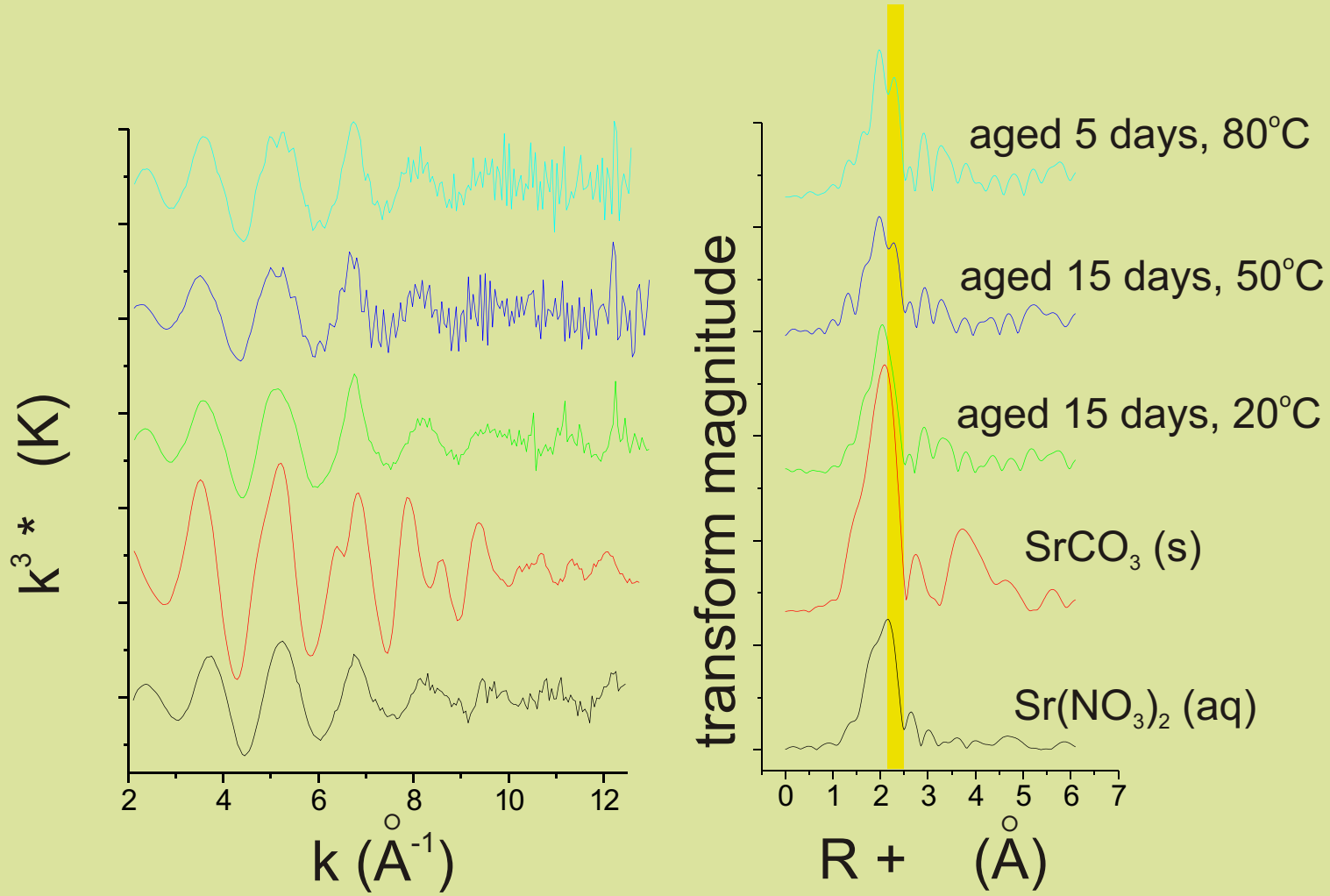


Figure 9. Sr K-edge EXAFS of sorbed Strontium on wet Al gels, aged under various conditions.

SUMMARY

- Aluminum hydroxide solids precipitated from solutions at different Al concentrations, pH values, and sodium nitrate concentrations are sensitive to the exact chemical and physical environment during precipitation and to the aging conditions after precipitation;

- XRD and Al K-edge XANES on air-dried and vacuum-dried samples indicate that boehmite precipitates initially but under certain conditions transforms to bayerite or gibbsite.

- Strontium sorbs significantly to Al hydroxide solids under a variety of solution conditions, especially as the pH is raised above 10;

- Strontium sorption to Al gels is greater than for Al hydroxide powders and becomes significant at lower pH values;

- Little difference is noted between Sr sorption on freshly-precipitated Al gels and Al gels that were aged for 5 days at 80° C;

- Strontium sorption on Al hydroxide powders is sensitive to the background electrolyte concentration ($NaNO_3$) - decreasing at high concentrations (> 0.3 *M* $NaNO_3$). At lower concentrations of $NaNO_3$ (< 0.3 *M* $NaNO_3$) at pH 10, the fraction of Strontium sorbed on boehmite, bayerite and gibbsite is above 98%. In 2 *M* $NaNO_3$ boehmite sorbs more Strontium (32%) than bayerite (13%) and gibbsite (0.3%);

- Sr K-edge EXAFS of Sr sorbed to Al gels shows a feature appearing during aging of the gels at 2.3 angstroms.

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